

METHOD FOR THE PRODUCTION OF FILM REAR-INJECTED PLASTIC MOLDED PARTS AND FILM REAR-INJECTED PLASTIC MOLDED PARTS

Specification

The present invention relates to a method for producing film rear-injected plastic molded parts, to these plastic molded parts, and to their use as interior or exterior auto body components, interior components for aircraft, interior components for ships, housings of household appliances and electric appliances, outdoor furniture, battery carriers, casement sections, curtain walls, doors, floor coverings, mobile telephone housings or shells for chairs.

Methods for the production of films reinforced with plastic material, or composite laminated films, are known to one skilled in the art. In European Patent Disclosure EP-A 0 285 071, for instance, a multi-layer foil comprising a clear layer, a colored layer, and a supporting layer is described, which is backed with a substrate material of unreinforced ABS polymer, polybutylene terephthalate, polyamide, polyethylene, or polypropylene. The clear layer used serves as a protective layer for the decorative layer and preferably comprises a mixture of a fluorinated polymer and an acrylic resin. The layered makeup of the composite laminated film is obtained, according to the method described, by means of film casting. Although composite shaped bodies are obtained in this way, nevertheless the production process necessitates drying steps and is technologically complicated and therefore labor-intensive and time-consuming. Moreover, the range of application of the shaped bodies obtained is necessarily quite limited, since no practicable access to fiber-reinforced composite molded parts is disclosed.

Producing a composite laminated film in accordance with European Patent Disclosure EP-A 0 352 298 proves to be similarly complicated. According to this reference, first a film composite comprising a colored layer and a clear layer is made from a cast film, which is then laminated to a substrate film by detaching the cast film from the clear layer with the side of the colored layer. In their composition, the individual film layers essentially correspond to those described in EP-A 0 285 071. Moreover, in EP-A 0 352 298, a plastic molding composition mixed with a filling material is disclosed that is used to reinforce the composite laminated film. However, this reinforced plastic molding composition does not have a flaw-free surface and must therefore be overcoated with the aforementioned composite laminated film. Another disadvantage is that even with the composite laminated film in place on top, irregularities in the surface of the reinforced plastic material cannot always be avoided or concealed entirely.

EP-A 0 442 128 discloses a simplified method for producing multi-layer molded parts

from a deformable film and thermosetting or pressure-setting plastic resins; in this method this heat-deformable film, for instance of polycarbonate which can also be printed on, is placed in the non-pre-deformed state in an injection molding tool and is both shaped and simultaneously kept in position by way of the pressure of the melted rear injection material.

Whether multi-layer composite films can also be processed satisfactorily into plastic molded parts by the method described is a question left unanswered, as is the question whether the positioning of the foil in the injection molding tool and the filling of this injection molding tool, also with fiber-reinforced plastic materials, are successfully accomplished. Moreover, EP-A 0 442 128 does not address the state in which the film has to be used.

In German Patent Application 109 28 774.0, rear-injected plastic molded parts which have a multi-layer composite film are accessible by providing that a multi-layer film comprising a cover layer and a decorative layer, optionally with an intermediate layer, is coextruded in a single process step and rear-injected directly afterward with a thermoplastic material. However, the molded parts thus obtained, for instance with a substrate layer of glass fiber reinforced PBT-ASA, do not always exhibit a satisfactory mechanical behavior required for all the desired uses, especially in terms of elongation to break and tensile strength. Moreover, if very long fiber materials are used, an unsatisfactory appearance may result after alternating temperature stresses, which precludes applications in the field of visible components such as exterior vehicle body parts. When glass fiber reinforced substrate rear injection compositions are used, and especially when long glass fibers are employed, so-called glass pits are often also observed on the surface of the molded parts obtained. These glass pits also not only adversely affect the appearance properties of the molded parts obtained but also locally affect their profile of mechanical properties. Even if it is successfully possible in the manner described to create molded parts that initially have satisfactory surfaces, roughness and possibly impairments in gloss and color cannot always be avoided in the climate change test, because of these glass pits.

It would therefore be desirable to obtain rear-injected composite molded parts that do not have the above disadvantages and that can be considered for the most manifold applications, both interior and exterior. It would also be advantageous if the underside or back side of a film rear-injected molded part had a uniform appearance that is free of glass pits or similar visible or perceptible residues of glass fiber, so that these components have a satisfactory appearance in every respect and even the back sides of these components can be placed where they can be seen, as in the case of housing lids or the outsides of hatchbacks.

It was therefore the object of the present invention to make a method for producing rear-injected plastic molded parts available in which, in a replicable and technologically simple way, film rear-injected plastic molded parts are obtained in which for the rear

injection, long-fiber-reinforced material is used and which meet the most stringent possible demands both mechanically and in terms of appearance.

Accordingly, a method for producing film rear-injected plastic molded parts from a film and a long-fiber-reinforced plastic material has been discovered in which the film is positioned in a forming tool and is rear-injected, with a plastic material reinforced with fiber material, to make a molded part; before the rear injection, the plastic material and the fiber material are placed, melted and mixed in an extruder or injection molding machine which at least in the zone adjoining the compression zone has at least one distributive mixing element.

The film rear-injected plastic molded parts produced by this method and their use as interior or exterior auto body components, interior components for aircraft, interior components for ships, housings of household appliances and electric appliances, outdoor furniture, battery carriers, casement sections, curtain walls, doors, floor coverings, mobile telephone housings or shells for chairs, have also been discovered.

The structure and composition of the film rear-injected plastic molded parts according to the invention and their production will be described in detail below.

As the films, both single-layer films and films with two or more layers can be considered. Preferably, films with two or more layers, that is, composite laminated films, will be used. Suitable single-layer films are formed for instance from mixtures of polyamides and polyethylene ionomers, such as ethene/methacrylic-acid copolymers, for instance containing counterions of sodium, zinc and/or lithium (obtainable on the market, among other sources under the trade name Surlyn®, made by DuPont), or from copolyesters. However, all the other currently used single-layer films can also be employed, such as PVC, ABS, ASA, polyester, or polycarbonate films. Composite laminated films composed of at least one substrate layer (1), optionally at least one intermediate layer or decorative layer (2), and at least one transparent cover layer (3), in that order, are especially suitable.

The substrate layer (1) generally includes thermoplastic polymers, such as ASA polymers, ABS polymers, polycarbonates, polyesters such as polyethylene terephthalate or polybutylene terephthalate, polyamides, polyether imides, polyether ketones, polyphenyl sulfides, polyphenylene ethers, or mixtures of these polymers.

For the substrate layer, ASA polymers are preferably used. The term ASA polymers is understood in general to mean styrene-acrylonitrile polymers with modified impact strength, in which graft copolymers of vinyl aromatic compounds, in particular styrene, and vinyl cyanides, in particular acrylonitrile, on polyalkyl acrylate rubbers (component A) in a

copolymer matrix, in particular of styrene and acrylonitrile (component B) are present. In a further preferred embodiment, blends of ASA polymers and polycarbonates are used. Particularly suitable ASA polymers are composed of a graft copolymer (component A) comprising

a1) 1 to 99 weight-%, preferably 55 to 80 weight-%, and in particular 55 to 65 weight-%, of a particulate graft foundation A1 with a glass transition temperature below 0°C, preferably below -20°C, and especially preferably below - 30°C,

a2) 1 to 99 weight-%, preferably 20 to 45 weight-%, and in particular 35 to 45 weight-%, of a graft overlay A2 comprising the following monomers, referred to A2,

a21) 40 to 100 weight-%, preferably 65 to 85 weight-%, units of styrene, of a substituted styrene, or of a (meth)acrylic acid ester, or mixtures therein, in particular of the styrene and/or α -methylstyrene, as component A21, and

a22) 0 to 60 weight-%, preferably 15 to 35 weight-%, units of acrylonitrile or methacrylonitrile, in particular acrylonitrile, as component A22.

The component A1 substantially comprises the following monomers

a11) 80 to 99.9 weight-%, preferably 95 to 99.9 weight-%, of at least one C₁ to C₈ alkyl ester of acrylic acid, preferably n-butyl acrylate and/or 2-ethylhexyl acrylate, as component A11,

a12) 0 to 20 weight-%, preferably 0.01 to 5.0 weight-%, of at least one polyfunctional cross-linking monomer, preferably diallyl phthalate and/or dihydrodicyclopentadienyl acrylate (DCPA), as component A12.

The acrylate rubbers A1 are preferably alkyl acrylate rubber from one or more C₁ to C₈ alkyl acrylates, preferably C₄ to C₈ alkyl acrylates, and preferably at least in part, butyl-, hexyl, octyl, and/or 2-ethylhexyl acrylate and in particular n-butyl and/or 2-ethylhexyl acrylate are used.

These acrylate rubbers A1 preferably contain from 0.01 to 20 weight-%, preferably 0.1 to 5 weight-%, referred to the total weight of A1, of bi- or polyfunctional monomers with a cross-linking effect (cross-linking monomers). Examples of these are monomers that contain two or more double bonds capable of copolymerization and that are preferably not conjugated in the 1,3- position. Suitable cross-linking monomers are for instance divinylbenzene, diallyl maleate, diallyl fumarate, diallyl phthalate, triallyl cyanurate, triallyl isocyanurate, tricyclodecenyl acrylate, dihydrodicyclopentadienyl acrylate, triallyl

phosphate, allyl acrylate, and allyl methacrylate. Dihydrocyclopentadienyl acrylate (DCPA) has proved to be an especially favorable cross-linking monomer (see German Patent DE-C 12 60 135). Up to 30 weight-%, in terms of the total weight of A1, of monomers that form "hard" polymers can also be incorporated by polymerization into the alkyl acrylate rubbers A1, examples being vinyl acetate, (meth)acrylonitrile, styrene, substituted styrene, methyl methacrylate, and/or vinyl ether.

In one embodiment of the invention, cross-linked acrylic acid ester polymers with a glass transition temperature below 0°C serve as the graft foundation A1. The cross-linked acrylic-acid ester polymers should preferably have a glass transition temperature below -20°C, and in particular below -30°C.

In a preferred embodiment, the graft foundation A1 is composed of from 15 to 99.9 and in particular 70 to 99.9 weight-% of C₁ to C₈ alkyl esters of acrylic acid, 0.1 to 5 and in particular 0.1 to 3 weight-% of cross-linking agents, and 0 to 49.9 and in particular 0 to 20 weight-% of one of the further monomers or rubbers listed.

Suitable monomers for forming the graft overlay A2, as component A21, are for instance styrene, substituted styrenes such as singly or multiply substituted alkyl and/or halogen styrenes, such as α-methylstyrene, and (meth)acrylic acid esters, such as methyl methacrylate, 2-ethylhexyl acrylate, and n-butyl acrylate, and in particular methyl methacrylate. As component A22, acrylonitrile and methacrylonitrile, and in particular acrylonitrile, can be considered.

The component A is preferably graft copolymers. In general, graft copolymers A have a mean particle size d₅₀ of from 50 to 1000 nm, and preferably 50 to 800 nm, and especially preferably 50 to 600 nm. Preferred particle sizes of the graft foundation A1 are in the range from 50 to 350 nm, preferably from 50 to 300 nm, and especially preferably from 50 to 250 nm.

The graft copolymer A can be constructed in a single stage or multiple stages; that is, the graft core is surrounded by one or more graft sheaths. As a rule, a plurality of graft sheaths are applied by grafting in stages to the rubber particles, and each graft sheath can have a different composition. In addition to the grafting monomers, polyfunctional monomers containing cross-linking or reactive groups can be jointly grafted on (see also EP-A 230 282, German Published, Examined Patent Disclosure DE-AS 36 01 419, and EP-A 269 861).

In a preferred embodiment, component A comprises a graft copolymer constructed in multiple stages; the graft stages are generally produced from resin-forming monomers and have a glass transition temperature T_g above 30°C, and

preferably above 50°C. The multi-stage construction serves the purpose, among others, of obtaining (partial) compatibility of the rubber particles A with the component B.

In a further preferred embodiment of the invention, the distribution of particle size in component A is bimodal; as a rule, from 60 to 90 weight-% has a mean particle size of 50 to 200 nm and from 10 to 40 weight-% has a mean particle size of 50 to 400 nm, referred to the total weight of component A.

The sizes determined from integral mass distribution are given as the mean particle size, or particle size distribution. The mean particle sizes according to the invention are in all cases the averaged weight of the particle sizes, as determined by means of an analytical ultracentrifuge using the method of W. Scholtan and H. Lange, in Kolloid-Z. und Z.-Polymere 250 (1972), pages 782 to 796. The ultracentrifuge measurement provides the integral mass distribution of the particle diameter of a sample. From that, it can be learned how high the weight-% is of the particles with a diameter equal to or less than a certain size. The mean particle diameter, which is also known as the d_{50} value of integral mass distribution, is defined as the particle diameter at which 50 weight-% of the particles have a smaller diameter than the diameter corresponding to the d_{50} value. Correspondingly, 50 weight-% of the particles then have a larger diameter than the d_{50} value. For characterizing the range of the particle size distribution of the rubber particles, not only the d_{50} value (mean particle diameter), but also the d_{10} and d_{90} values from integral mass distribution are used. The d_{10} and d_{90} values from integral mass distribution are defined similarly to the d_{50} value, with the distinction that they are referred to 10 and 90 weight-% of the particles, respectively. The quotient $(d_{90} - d_{10})/d_{50}$ is a measure of the range of distribution of the particle size. The lower Q is, the narrower the distribution is.

The graft copolymers A can be produced by means of emulsion polymerization, solution polymerization, mass polymerization, or suspension polymerization. Radical emulsion polymerization is preferred, in which in the presence of lattices of component A1, at temperatures up to 90°C, the monomers A21 and A22 are grafted on using water- or oil-soluble initiators, such as peroxide sulfate or benzyl peroxide, or with the aid of redox initiators. Redox initiators can also be used for polymerizations below 20°C.

Suitable emulsion polymerization methods are described for instance in German Patent Disclosures DE-A 28 26 925 and DE-A 31 49 358 and in German Patent DE-C 12 60 135.

The graft sheath construction by means of emulsion polymerization is also described in DE-A 32 27 555, DE-A 31 49 357, DE-A 31 49 358, and DE-A 34 14 118. The particle size of component A can be adjusted, in particular including to values in the range from 50 to 1000 nm, preferably by the methods disclosed in DE-C 12 60 135, DE-A 28 26 925, and

in Applied Polymer Science, Vol. 9 (1965), page 2929. Polymers with different particle size distributions can be produced for instance in accordance with DE-A 28 26 925 and US Patent 5,196,480.

For example, by the method described in DE 12 60 135, first the graft foundation A1 can be obtained by polymerizing C₁ to C₈ alkyl esters of acrylic acid and cross-linking monomers, optionally along with further comonomers, in aqueous solution in a manner known per se at temperatures between 20 and 100°C, and preferably between 50 and 80°C. The usual emulsifiers can be employed, such as alkaline salts of alkyl or alkylaryl sulfonic acids, alkyl sulfates, fatty alcohol sulfonates, salts of higher fatty acids with from 10 to 30 carbon atoms, or resin soaps. Preferably, sodium salts of alkyl sulfonates or fatty acids with from 10 to 18 carbon atoms are used. In one embodiment, the emulsifiers are added in quantities of 0.5 to 5 weight-%, and in particular from 1 to 10 weight-%, referred to the monomers used in producing the graft foundation A1. In general, work is done with a weight ratio of water to monomer of 2:1 to 0.7:1. As polymerization initiators, the usual peroxosulfates, such as potassium peroxosulfate, are used in particular. However, redox systems can also be employed. The initiators are generally added in quantities of from 0.1 to 1 weight-%, referred to the monomers employed in producing the graft foundation A1. As further polymerization adjuvants, typical buffer substances can also be used, such as sodium bicarbonate or sodium pyrophosphate, with which pH values of preferably 6 to 9 are established, as well as from 0 to 3 weight-% of a molecular weight regulator, such as mercaptans, terpinols, or dimeric α-methylstyrene.

The latex of cross-linked acrylic acid ester polymer obtained is, in one embodiment of the invention, grafted with a monomer mixture of a vinyl aromatic compound (component A21), such as styrene, and a vinyl cyanide (component A22), such as acrylonitrile; the weight ratio, for instance of styrene to acrylonitrile in the monomer mixture, is in the range from 100:0 to 40:60, and preferably in the range from 65:35 to 85:15. Advantageously, this graft copolymerization is again performed in aqueous emulsion under the usual conditions described above. The graft copolymerization can expediently be done in the same system as the emulsion polymerization for producing the graft foundation A1; if necessary, further emulsifiers and/or initiators can be added. The monomer mixture of styrene and acrylonitrile can be added to the reaction mixture all at once, or in batches in several stages, or preferably continuously during the polymerization. The graft copolymerization of this mixture in the presence of the cross-linked acrylic-acid ester polymer is preferably done such that the resultant grafting degree in the graft copolymer A is 1 to 99 weight-%, preferably 20 to 45 weight-%, and in particular 35 to 45 weight-%, referred to the total weight of component A. Since as a rule the graft yield in graft copolymerization is not 100%, a somewhat greater quantity of the monomer mixture of styrene and acrylonitrile than is needed for the desired grafting degree is often used in graft copolymerization. Controlling the graft yield in graft copolymerization and thus the graft

proportion of the finished graft copolymer A is familiar to one skilled in the art and can be accomplished, among other ways, by means of the metering speed of the monomer or by adding regulators (Chauvel, Daniel, ACS Polymer Preprints 15 (1974), page 329 ff.). In emulsion graft copolymerization, generally approximately 5 to 15 weight-%, referred to the graft copolymer A, of free or in other words ungrafted styrene-acrylonitrile copolymer occurs. The proportion of the graft copolymer A in the polymerization product obtained in the graft copolymerization is ascertained by the method described above.

In the production of the graft copolymer A by the emulsion process, along with the advantages in terms of method given, replicable particle size changes are also possible, for instance by means of at least partial agglomeration of the particles to form larger particles. This means that even polymers with different particle sizes can be present in the graft copolymer A.

Component B is a copolymer, which essentially contains

- b1) 40 to 100 weight-%, preferably 60 to 85 weight-%, units of styrene, a substituted styrene, or a (meth)acrylic acid ester, or mixtures thereof, and in particular styrene and/or α -methylstyrene as component B1, and
- b2) from 0 to 60 weight-%, preferably 15 to 40 weight-%, units of acrylonitrile or methacrylonitrile, in particular acrylonitrile, as component B2.

In a preferred embodiment of the invention, the coefficient of viscosity of component B is from 50 to 90, and preferably 60 to 80, determined in accordance with DIN 53726, in a 0.5 weight-% solution in dimethyl formamide.

Preferably component B is an amorphous polymer, for instance as described above as the graft overlay A2. In one embodiment of the invention, a copolymer of styrene and/or α -methylstyrene with acrylonitrile is used as component B. The acrylonitrile content in these copolymers of component B is generally from 0 to 60 weight-%, preferably 15 to 40 weight-%, referred to the total weight of component B. Included in component B are also the free, ungrafted copolymers of vinyl aromatic compounds and vinyl cyanides, such as styrene-acrylonitrile copolymers, that occur in the graft copolymerization for producing component A. Depending on the conditions chosen in the graft copolymerization for producing the graft copolymer A, it can be possible for a sufficient proportion of component B to have already been formed in the graft copolymerization. In general, however, it is necessary for the products obtained in the graft copolymerization to be mixed with additional, separately produced component B. It is understood that the components A2 and B need not match in terms of their composition.

This additional, separately produced component B is preferably a styrene-acrylonitrile copolymer, an α -methylstyrene-acrylonitrile copolymer, or an α -methylstyrene-styrene-acrylonitrile terpolymer. These copolymers can be used individually or as a mixture for component B, so that the additional, separately produced component B can for instance be a mixture of a styrene-acrylonitrile copolymer and an α -methylstyrene-acrylonitrile copolymer. In the case in which component B comprises a mixture of a styrene-acrylonitrile copolymer and an α -methylstyrene-acrylonitrile copolymer, the acrylonitrile content of the two copolymers should preferably not deviate from one another by more than 10 weight-%, and preferably no more than 5 weight-%, referred to the total weight of the copolymer. However, the component B can also comprise only a single copolymer of vinyl aromatic compounds and vinyl cyanides, if the starting mixture both in the graft copolymerization for producing component A and in the preparation of the additional, separately produced component B is the same monomer mixture.

The additional, separately produced component B can be obtained by the conventional methods. In one embodiment of the invention, the copolymerization, for instance of styrene and/or α -methylstyrene with acrylonitrile, can be performed in bulk, in solution, in suspension, or in aqueous emulsion.

In a preferred embodiment, the substrate layer (1) contains not only components A and B but, as additional components, polycarbonates and optionally further additives, as described below.

Suitable polycarbonates are known per se. The term polycarbonates in the context of the invention predominantly includes copolycarbonates. Polycarbonates preferably have a molecule weight (mean weight value M_w , determined by gel permeation chromatography in tetrahydrofuran, in comparison to polystyrene standards) in the range from 10000 to 200000 g/mol. Preferably, they are in the range from 15000 to 100000 g/mol. This means that the polycarbonates in general have relative solution viscosities in the range from 1.1 to 1.5, measured in 0.5 weight-% solution in dichloromethane at 25°C, and preferably from 1.15 to 1.33.

Polycarbonates can be obtained for instance by the method of German Patent Disclosure DE-B 1 300 266 by boundary face polycondensation, or by the method of DE-A 1 495 730 by conversion of diphenyl carbonate with bisphenols. A preferred bisphenol is 2,2-di(4-hydroxyphenyl)propane, which is generally - and hereinafter - called bisphenol A. Examples of commercially available polycarbonates are Makrolon® (Bayer) and Lexan® (GE Plastics).

Instead of bisphenol A, other aromatic dihydroxy compounds can be used, in particular 2,2-di(4-hydroxyphenyl)pentane, 2,6-dihydroxynaphthalene, 4,4'-dihydroxydiphenyl

sulfone, 4,4'-dihydroxydiphenyl ether, 4,4'-dihydroxydiphenyl sulfite, 4,4'-dihydroxydiphenyl methane, 1,1-di-(4-hydroxyphenyl)ethane, 4,4-dihydroxydiphenyl or dihydroxydiphenyl cycloalkanes, and preferably dihydroxydiphenyl cyclohexanes or dihydroxy cyclopentanes, in particular 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane, and mixtures of the aforementioned dihydroxy compounds.

Especially preferred polycarbonates are those based on resorcinol or resorcinol arylates, and on the basis of bisphenol A, or bisphenol A together with up to 80 mol-% of the aforementioned aromatic dihydroxy compounds. It is also possible to use copolycarbonates in accordance with US Patent 3,737,409. Of particular interest are copolycarbonates on the basis of bisphenol A and bis-(3,5-dimethyl-4-hydroxyphenyl)sulfone and 1,1-di-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexyl, which are distinguished by a high heat distortion point. This last copolycarbonate is also commercially available under the trade name Apec®HT (Bayer). It is also possible to use mixtures of different polycarbonates.

The polycarbonates can be used both as a ground product or in granulated form. In the ASA substrate layer, they are typically present in quantities of from 0 to 50 weight-%, preferably from 10 to 40 weight-%, in each case referred to the entire molding composition.

The addition of polycarbonates leads, among other effects, to greater thermal stability and improved resistance to cracking of the composite laminated films.

Mixing the components A, B and optionally the polycarbonates can be done in any arbitrary way, using all known methods. For instance, if components A and B were produced by emulsion polymerization, it is possible to mix the polymer dispersions obtained together, then to precipitate the polymers out jointly, and to process the polymer mixture. Preferably, however, the mixing of components A and B is done by coextrusion, kneading, or rolling of the components, preferably at temperatures in the range from 180 to 400°C, the components having been isolated, if necessary, beforehand from the solution or aqueous dispersion obtained in the polymerization. The products of the graft copolymerization (component A) obtained in aqueous dispersion can also be dewatered only partly and mixed in the form of moist crumbs with the component B; in that case, the complete drying of the graft copolymers is effected during the mixing.

It can be advantageous to premix individual components. It is also possible to mix the components in solution and remove the solvent. Organic solvents, such as chlorobenzene, mixtures of chlorobenzene and methylene chloride, or mixtures of chlorobenzene or aromatic hydrocarbons, such as toluene, are preferred. The evaporative concentration of the solvent mixtures can for instance be done in evaporative concentration extruders. The

components can be metered in either together or separately/sequentially.

The substrate layer (1) of components A, B and optionally polycarbonates can further contain, as further additives, such compounds as are typical and usual for the (co)polymers described, such as polycarbonates, SAN polymers, or graft copolymers, and mixtures thereof. Examples of additives that can be named are: dyes, pigments, effect colorants, antistatic agents, antioxidants, stabilizers for improving thermal stability, increasing lightfastness, and raising the resistance to hydrolysis and chemical resistance, and means to counter thermal decomposition and in particular lubricants, which are expedient for producing molded bodies or molded parts. Metering in these further additives can be done in any stage of the production process, but preferably at an early time, in order to make early utilization of the stabilizing effects (or special effects) of the additive. Heat stabilizers and oxidation retardants are typically metal halides (chlorides, bromides, iodides), which are derived from metals of group I of the periodic system of elements (such as lithium, sodium, and potassium).

Suitable stabilizers are the usual hindered phenols, such as 2,6-disubstituted phenols like bis(2,6-tert-butyl)-4-methylphenol (BHT), 4-methoxymethyl-2,6-di-tert-butylphenol, 2,6-di-tert-butyl-4-hydroxymethylphenol, 2,2-bis-(4-hydroxyphenyl)propane, 4,4'-dihydroxybiphenyl and bis(2,6-methyl)-4-methylphenol, and bis(2,6-(C₁ to C₁₀ alkyl)-4-(C₁ to C₁₀ alkyl)phenols are preferred. Vitamin E, or analogously constructed compounds, can also be considered. So-called HALS stabilizers (hindered amine light stabilizers), such as tetraalkyl piperidine-N-oxy compounds, benzophenones, resorcins, salicylates and benzotriazoles are also suitable, such as Tinuvin® P (2-(2H-benzotriazol-2-yl)-4-methylphenol). These are typically used in quantities of up to 2 weight-%, referred to the total weight.

Suitable lubricants and unmolding agents are stearic acids, stearyl alcohol, stearic acid esters and in general higher fatty acids, their derivatives, and corresponding fatty acid mixtures with from 12 to 30 carbon atoms. The quantities of these additives are in the range from 0.05 to 1 weight-%, referred to the total weight.

Silicone oils, oligomeric isobutylene or similar substances can also be considered as additives; the usual quantities are from 0.05 to 5 weight-%, referred to the total mixture. Pigments, dyes, optical brighteners, effect colorants such as titanium dioxide, soot, iron oxides, phthalocyanines, quinacridones, perylenes, anthraquinones, and aluminum flit can also be used.

Processing aids, such as lubricants, and stabilizers, such as UV stabilizers, as well as antistatic agents are typically used together in quantities of from 0.1 to 5 weight-%.

Instead of ASA polymers or blends of them with polycarbonates, or in addition to the latter, the substrate layer (1) can also contain ABS polymers (which means among others modified high-impact styrene-acrylonitrile polymers, in which graft copolymers of styrene and acrylonitrile are present on polybutadiene rubbers in a copolymer matrix of styrene and acrylonitrile), polycarbonates, polyesters such as polybutylene terephthalate (PBT) or polyethylene terephthalate (PET), polyamides, polyether imides (PEI), polyether ketones (PEK), polyphenylene sulfides (PPS), polyphenylene ethers, or blends of these polymers. The aforementioned polymer materials are widely known, for instance from H.

Domininghaus, Die Kunststoffe und ihre Eigenschaften [Plastics and their Properties], VDI-Verlag, Düsseldorf (1992).

In a preferred embodiment, the substrate layer (1) is formed from ASA polymers, mixtures of ASA polymers and polycarbonates, ABS polymers, polycarbonates, polybutylene terephthalate, polyethylene terephthalate, polyamides, or blends of ASA polymers and polybutylene terephthalate. Especially preferably, the substrate layer (1) includes a molding composition of ASA polymers or mixtures of ASA polymers and polycarbonates. It can also substantially or entirely comprise these polymers.

The layer thickness of the substrate layer (1) is preferably 100 to 2000 µm, in particular 150 to 1500 µm, and especially preferably 200 to 1000 µm.

The composite laminated films, in a further embodiment, have an intermediate layer (2) of thermosetting and/or pressure-setting plastics, optionally with further additive substances and/or additives. Suitable thermosetting plastics are for instance the polyalkyl and/or aryl esters of (meth)acrylic acid, poly(meth)acrylamide, or poly(meth)acrylonitrile, also known as acrylic resins, as well as ABS polymers, styrene-acrylonitrile polymers (SAN), polycarbonates, polyesters such as polyethylene terephthalate or polybutylene terephthalate, polyamides, in particular amorphous polyamide, such as polyamide 12, polyether sulfones, thermoplastic polyurethanes, polysulfones, polyvinyl chloride, or ASA polymers. Blends of the above (co)polymers are also fundamentally suitable, such as mixtures of ASA polymers and polycarbonates, as described above for the substrate layer (1). Thermoplastic polyurethanes, in particular weather-resistant aliphatic polyurethanes, such as the commercial product Elastollan® (Elastogran, Lemförde) (see also Kunststoff-Handbuch, Polyurethane [Plastics Handbook, Polyurethanes], Vol. 7, 2nd Ed., Carl Hanser Verlag, München, 1983, pp. 31-39) can be considered as film materials. Acrylic resins, polycarbonates, and/or styrene (co)polymers are preferably used.

Included among suitable acrylic resins are poly(meth)acrylates, that is, esters of acrylic acid and methacrylic acid, and mixtures of these polymers, or copolymers of acrylates and methacrylates. Preferably, polyalkyl methacrylates, including those in modified high-impact form, especially polymethyl methacrylate (PMMA) or modified high-impact

polymethyl methacrylate (HI-PMMA), are used. In a preferred embodiment, PMMA includes a proportion of as a rule no more than 20 weight-% of (meth)acrylate comonomers, such as n-butyl (meth)acrylate or methyl acrylate. High-impact PMMA (HI-PMMA) is a polymethyl methacrylate that is made to be high-impact by means of suitable additives. As impact-strength modifiers, EPDM rubbers, polybutyl acrylates, polybutadiene, polysiloxane, or methacrylate-butadiene-styrene (MBS) and methacrylate-acrylonitrile-butadiene-styrene copolymers, for instance, can be considered. Suitable modified high-impact poly(meth)acrylates are described for instance in M. Stickler and T. Rhein in Ullmann's Encyclopedia of Industrial Chemistry, Vol. A21, pp. 473-486, VCH publishers, Weinheim, 1992 and H. Domininghaus, Die Kunststoffe und ihre Eigenschaften [Plastics and their Properties], VDI-Verlag, Düsseldorf (1992). Suitable polymethyl methacrylates are furthermore known to one skilled in the art and can be obtained for instance by the trademarks Lucryl® (BASF AG) and Plexiglas® (Röhm GmbH).

Polyesters are understood to be the higher- to high- molecular-weight products of esterification of divalent acids, in particular terephthalic acid, with divalent alcohols, above all ethylene glycol. Among the polyalkylene terephthalates, polyethylene terephthalate (PET) is especially suitable. Commercial PET products are for instance Arnite® (Akzo), Grilpet® (EMS-Chemie) and Valox® (GE Plastics).

Thermoplastic polyurethanes (TPU), finally, are the reaction products of diisocyanates with long-chained diols. Compared to the polyurethane foams obtained from polyisocyanates (containing at least three isocyanate groups) and multivalent alcohols (containing at least three hydroxy groups), in particular polyether and polyester polyols, thermoplastic polyurethanes have no cross-linking, or only slight cross-linking, and accordingly have a linear structure. Thermoplastic polyurethanes are well known to one skilled in the art and are described for instance in Kunststoff-Handbuch [Plastics Handbook], Vol. 7, Polyurethane [Polyurethanes], edited by G. Oertel, 2nd Ed., Carl Hanser Verlag, München, 1983, especially on pp. 428-473. As an example of a commercially available product, Elastollan® (Elastogran GmbH) can be named here.

Examples of suitable pressure-setting plastics are polyurethane foams, for instance the so-called polyester foam materials and especially polyether foam materials. This class of compounds is well known to one skilled in the art and is described, among other places, in Kunststoff-Handbuch [Plastics Handbook], Vol. 7, Polyurethane [Polyurethanes], edited by G. Oertel, 2nd Ed., Carl Hanser Verlag, München, 1983, particularly on pp. 170-246.

Preferably, acrylic resins and/or styrene (co)polymers will be used .

The intermediate layer (2) can also serve as a dye vehicle or decorative layer. It is

preferably constructed of high-impact polymethyl methacrylates (PMMA), polycarbonates, or the ASA polymer as described above for the substrate layer (1), or blends of them with polycarbonates. The intermediate layer (2) can also contain effect colorants. These are for instance dyes, metal flecks, or pigments. Organic or inorganic compounds can be considered as dyes or pigments. Multicolored, white and black pigments (colored pigments) and liquid crystal pigments can be named as organic pigments. Once again both colored pigments and gloss pigments and the usual inorganic pigments used as fillers are suitable as inorganic pigments. It is understood that various organic, inorganic, or combinations of organic and inorganic pigments can also be used.

In a further embodiment, the substrate layer (1) - alone or together with an optionally present intermediate layer (2) - has the aforementioned effect colorants.

The layer thickness of the decorative layer (2) is generally in the range from 10 to 1000, preferably 50 to 500, and especially preferably 100 to 400 μm .

For the cover layer (3) of the composite laminated films, poly(meth)acrylate polymers are typically used. Polymethyl methacrylates (PMMA) are especially suitable as cover layer material, for instance as described in EP-A 0 255 500. PMMA with mean molecular weights in the range from 40000 to 100000 g/mol is preferred. Suitable PMMA molding compositions are for instance products that can be obtained under the tradename Lucryl® (BASF AG).

As a rule, the cover layer (3) is translucent, and preferably transparent. Instead of poly(meth)acrylate polymers, or together with them, high-impact poly(meth)acrylates can also be used, especially high-impact polymethyl methacrylate, fluoro(co)polymers such as polyvinylidene fluoride (PVDF), ABS polymers, polycarbonates, polyethylene terephthalate, amorphous polyamide, polyether sulfones, polysulfones, or SAN copolymers. In particular, the cover layer contains polymethyl methacrylate, high-impact polymethyl methacrylate, or polycarbonates, preferably polymethyl methacrylate, high-impact polymethyl methacrylate, PVDF, or mixtures thereof. The polymers and their mixtures are as a rule selected such that they lead to a transparent cover layer.

Suitable fluoro(co)polymers are formed of olefinically unsaturated monomers and comonomers, in which at least one SP^2 carbon is covalently linked with at least one fluorine atom. These (co)monomers include for instance chlorotrifluoroethene, fluorovinylsulfonic acid, hexafluoroisobutene, hexafluoropropene, perfluorovinyl methyl ether, tetrafluoroethene, and vinyl fluoride, and in particular vinylidene fluoride. The mean molecular weight of fluoro(co)polymers is typically in the range from 50000 to 300000, and preferably in the range from 100000 to 200000 g/mol. Mixtures of fluoro(co)polymers and poly(meth)acrylates can also be used. Mixtures of polyvinylidene fluoride (PVDF) and

polymethyl methacrylate are preferred. The proportion of PVDF in these mixtures is advantageously in the range from 40 to 80 and preferably 55 to 75 weight-%, referred to the total weight of the mixture.

In a further embodiment, the cover layer originates in a radiation-curable composition, which contains functional groups that can be cured both ionically and in particular radically. The radically radiation-curable cover layer includes preferably i) polymers with ethylenically unsaturated groups or ii) mixtures of these polymers with ethylenically unsaturated low-molecular compounds or iii) mixtures of thermosetting plastics without ethylenically unsaturated groups with ethylenically unsaturated compounds.

In polymer i), for ethylenically unsaturated groups, it is possible for instance to use maleic acid, fumaric acid, maleic acid anhydride, or (meth)acrylic acid radicals. Suitable polymers i) can be based on polyesters, polyethers, polycarbonates, polyepoxides, or polyurethanes.

As ethylenically unsaturated low-molecular compounds, the following can for instance be considered: alkyl (meth)acrylates, such as methyl methacrylate, methyl acrylate, n-butyl acrylate, ethyl acrylate, or 2-ethylhexyl acrylate; vinyl aromatic compounds, such as vinyl toluene or styrene; vinyl esters, such as vinyl stearate or vinyl acetate; vinyl ethers, such as vinyl methyl ether, acrylonitrile, or methacrylonitrile.

Suitable saturated thermoplastic polymers are for instance polymethyl methacrylate, high-impact polymethyl methacrylate, polystyrene, high-impact polystyrene (HIPS), polycarbonate, or polyurethanes.

The radiation-curable composition can also contain, as further ingredients, photoinitiators, flow-control agents, or stabilizers, such as UV absorbers and radical absorbers.

The radiation curing of the cover layer is done with high-energy radiation, such as UV light or electron radiation, optionally at elevated temperatures.

For further details of the composition of the radiation-curable cover layer and its production, WO 00/63015 is expressly referred to here.

An adhesive layer of an adhesion promoter, with a layer thickness of in general 5 to 400 and in particular 5 to 100 μm can adjoin the outer surface of the substrate layer. The adhesion promoter serves to establish a solid connection with a selected substrate that comes to be located below the substrate layer (for instance as a result of rear injection). The adhesion layer is used whenever the adhesion of this further substrate to the substrate layer

is inadequate (for instance in the case of polyolefin substrates). Suitable adhesion promoters are known to one skilled in the art. Examples of suitable adhesion promoters are ethylene vinyl acetate copolymers for coupling to polyethylene, and maleic acid anhydride-grafted polypropylenes for coupling to polypropylene. In both cases, according to current thinking, the adhesion is achieved by incorporating polar groups into the nonpolar polyolefins.

Rear-injected or composite laminated films comprising a substrate layer (1), optionally an intermediate layer or decorative layer (2), a cover layer (3), and optionally an adhesion layer (0) typically have the following layer thicknesses:

substrate layer (1): 100 to 2000 μm , preferably 150 to 1500 μm , and especially preferably 200 to 1000 μm ;

intermediate layer (2): 0 to 1000 μm , preferably 50 to 500 μm , especially preferably 70 to 400 μm , and in particular from 100 to 300 μm ;

cover layer (3): 20 to 300 μm , preferably 50 to 200 μm , and especially preferably 50 to 100 μm ; and

adhesion layer (0): 0 to 400 μm , preferably 10 to 200 μm , and especially preferably 50 to 100 μm .

The total thickness of this composite laminated film is typically in the range from 150 to 2000 μm , preferably 250 to 1500 μm , and especially preferably 200 to 1000 μm .

A three-layer film can for instance be produced beginning with a composite laminated film comprising the two layers (2) and (3), by retroactively providing them with a substrate layer (1). For producing the composite laminated film, it is as a rule advantageous for the ratio of magnitude of the MFI (melt flow index) values of the individual components of the composite laminated films to be at most 3:1, and especially preferably at most 2:1. Thus the highest MFI value of one of the components (0), (1), (2), (3), if present in the respective composite laminated films, amounts to at most three times and especially preferably at most twice the lowest MFI value. As a result, a uniform flow behavior of all the components used in the composite layer plates or composite laminated films is assured. This flow behavior adapted to one another is particularly advantageous if the composite laminated films are produced by adaptor coextrusion or nozzle coextrusion of the components. Preferably the entire composite is produced in a single-stage process. Particularly in adaptor coextrusion methods, adaptation of the flow properties of the individual components is advantageous for the sake of embodying uniform layers.

Nozzle coextrusion, particularly utilizing "diaphragm nozzle technology" has the advantage for example of enabling higher orientation of metal glitter and thus an improved appearance of a metallic paint. The individual components are made flowable in extruders and are put into contact with one another via special devices in such a way that composite laminated films with the above-described layer sequence result. For instance, the components can be coextruded through a wide-slot nozzle. This method is explained for instance in EP-A2 0 225 500.

The production of composite laminated films by the adaptor coextrusion process is described for instance in the conference proceedings of the Extrusionstechnik [Extrusion Technology] Conference entitled "Coextrusion von Folien" [Coextrusion of Films], October 8 and 9, 1996, VDI-Verlag Düsseldorf, and in particular in the paper by Dr. Netze. This commercial method is used in most coextrusion applications.

The composite laminated films can also be produced laminating the individual film layers to one another in a heatable gap. First, films are made from the individual components. This can be done by known methods. Next, the desired layer sequence is produced by suitably stacking the films, and then they are passed through a heatable roller gap and bonded under the influence of pressure and heat to form a composite layer plate or composite laminated film.

A protective layer, for instance of a polyethylene film, can also be applied, preferably temporarily, to one surface of the film layer. Advantageously, the protective layer is applied by means of known laminating or lining methods immediately after the film layer has been produced, for instance after the a multi-layer film comprising a substrate layer, optionally a decorative layer, and a cover layer has been coextruded onto the still-warm top side of the film. This protective layer can be removed again at any arbitrary time in production or further processing of the composite film or of the rear injection/back-pressed molded part.

The production of molded parts, especially motor vehicle parts such as fenders, door panels, bumpers, spoilers, and outside mirrors, from the composite laminated films can be done by known methods. For instance, composite laminated films with the three-layer structure comprising a substrate layer, intermediate layer and cover layer, or the two-layer structure comprising a substrate layer and a cover layer can be preshaped by thermoforming. Either positive or negative thermoforming methods can be employed. Suitable methods are known to one skilled in the art. The composite laminated films of the invention are stretched here by the thermoforming method. Since the gloss or surface quality of the composite laminated films of the invention does not decrease with the stretching at high stretching ratios such as up to 1:5, the thermoforming methods have virtually no relevant limitations in practice with respect to the possible stretching.

By rear injection of the composite laminated films with a fiber-reinforced plastic material, the molded parts according to the invention are obtained. As the plastic materials, thermoplastic molding compositions on the basis of ASA polymers or ABS polymers, SAN polymers, poly(meth)acrylates, polyether sulfones, polyamides, polybutylene terephthalate, polycarbonates, polypropylene (PP) or polyethylene (PE), as well as blends of ABS polymers or ASA polymers and polycarbonates or polybutylene terephthalate and blends of polycarbonates and polybutylene terephthalate are preferably used; if PE and/or PP is used, it is attractive to provide the substrate layer with an adhesive layer (0) beforehand. Amorphous thermoplastics and blends thereof are especially well suited. Preferably, ABS polymers and their blends, for instance with polycarbonates, polybutylene terephthalate, or polyamides, are used as plastic material for the rear injection.

Especially suitable ABS polymers include the following components:

A') 5 to 70, preferably 8 to 65 weight-% of at least one graft copolymer A'), referred to A');

a1') 10 to 90 weight-% of at least one rubber-elastic graft foundation with a glass transition temperature below 0°C, obtainable by polymerization of the following, referred to a1'):

a11') 60 to 100, preferably 70 to 100 weight-% of at least one conjugated diene and/or C₁ to C₁₀ alkyl acrylate, in particular butadiene, isoprene, n-butyl acrylate, and/or 2-ethylhexyl acrylate;

a12') 0 to 30, preferably 0 to 25 weight-% of at least one further monoethylenically unsaturated monomer, in particular styrene, α-methylstyrene, n-butyl acrylate, methyl methacrylate, or mixtures thereof, the latter in particular including butadiene-styrene and n-butyl acrylate-styrene copolymers; and

a13') 0 to 10, preferably 0 to 6 weight-% of at least one cross-linking monomer, preferably divinylbenzene, diallyl maleate, allyl ester of (meth)acrylic acid, dihydronyclopentadienyl acrylate, divinyl esters of dicarboxylic acids such as succinic acid and adipic acid, and diallyl and divinyl ethers of bifunctional alcohols, such as ethylene glycol or butane-1,4-diol;

a2') 10 to 60, preferably 15 to 55 weight-% of a graft overlay a2'), referred to a2')

a21') 50 to 100, preferably 55 to 90 weight-% of at least one vinyl aromatic monomer,

preferably styrene and/or α -methylstyrene;

a22') 5 to 35, preferably 10 to 30 weight-% of acrylonitrile and/or methacrylonitrile, preferably acrylonitrile;

a23') 0 to 50, preferably 0 to 30 weight-% of at least one further monoethylenically unsaturated monomer, preferably methyl methacrylate and n-butyl acrylate; and

B') 29 to 90, preferably 34 to 88 weight-% of a hard copolymer, referred to B');

b1') 50 to 100, preferably 55 to 90 weight-% of at least one styrene compound, in particular styrene and/or α -methylstyrene;

b2') 0 to 50 weight-% of acrylonitrile or methacrylonitrile, or mixtures thereof;

b3') 0 to 50 weight-% of at least one further monoethylenically unsaturated monomer, such as methyl methacrylate and N-alkyl or N-aryl maleimides, such as N-phenyl maleimide.

These ABS polymers can also contain three-block copolymers EO-PO-EO, with a little block PO of propylene oxide units and terminal blocks EO of ethylene oxide units, such as the commercial product Pluronic® (BASF).

As stabilizers, the ABS polymers can also include butylated reaction products of p-cresol with dicyclopentadiene, for instance the commercial product Wingsty®L (Goodyear); thiocarboxylic acid esters such as thiodipropionic acid dilauryl ester (such as Cyanox® LTPD from American Cyanamid) and alkaline or alkaline-earth metal salts of a C₆ to C₂₀ carboxylic acid, such as magnesium or potassium stearate.

The production and both general and special embodiments of the aforementioned ABS polymers are described at length in German Patent Application DE 100 26 858.7, which had not yet been published by the priority date of the present application and is hereby expressly incorporated by reference.

ABS polymers, in a further, preferred embodiment, originate in the following:

A") 5 to 80, preferably 10 to 70 weight-% of a graft polymer A") with bimodal particle size distribution, referred to A");

a1") 40 to 90, preferably 45 to 85 weight-% of a rubber-elastic particulate graft foundation a1'), which can be obtained by polymerization of the following, referred to a1"):

a11") 70 to 100, preferably 75 to 100 weight-% of at least one conjugated diene, in particular butadiene and/or isoprene;

a12") 0 to 30, preferably 0 to 25 weight-% of at least one further monoethylenically unsaturated monomer, in particular styrene, α -methylstyrene, n-butyl acrylate, or mixtures thereof;

a2") 10 to 60, preferably 15 to 55 weight-% of a graft overlay a2"), referred to a2');

a21") 65 to 95, preferably 70 to 90 weight-% of at least one vinyl aromatic monomer, preferably styrene;

a22") 5 to 35, preferably 10 to 30 weight-% of acrylonitrile;

a23") 0 to 30, preferably 0 to 20 weight-% of at least one further monoethylenically unsaturated monomer, preferably methyl methacrylate and n-butyl acrylate; and

B") 20 to 95, preferably 30 to 90 weight-% of a thermoplastic polymer B") with a coefficient of viscosity (ascertained by DIN 53726 at 25°C in 0.5 weight-% solution in dimethyl formamide) of 50 to 120 ml/g, referred to B");

b1") 69 to 81, preferably 70 to 78 weight-% of at least one vinyl aromatic monomer, preferably styrene and/or α -methylstyrene;

b2") 19 to 31, preferably 22 to 30 weight-% of acrylonitrile;

b3") 0 to 30, preferably 0 to 28 weight-% of at least one further monoethylenically unsaturated monomer, such as methyl methacrylate or N-alkyl or N-aryl maleinimides, such as N-phenyl maleinimide.

In one embodiment, components B") that differ from one another in their coefficients of viscosity by at least 5 units (ml/g) and/or in their acrylonitrile contents by 5 units (in weight-%) are present side by side in the ABS polymers. In some parts, material of component B") can also be present, along with the molding composition described in B"), in which the acrylonitrile content is above 31 weight-%, and in particular is up to 37 weight-%. Finally, besides component B") and the other embodiments, copolymers of styrene and maleic acid anhydride or maleinimides, of styrene, maleinimides and methyl methacrylate or acrylonitrile, or of styrene, maleinimides, methyl methacrylate and acrylonitrile can also be present.

In these ABS polymers, the graft polymers A') and A") are preferably obtained by emulsion polymerization. Mixing the graft polymers A')/A") with the components B') and B"), and optionally further additives, is done in a mixing device, producing an essentially melted polymer mixture. It is advantageous for the molten polymer mixture to be cooled down as fast as possible.

Otherwise, the production and both general and special embodiments of the aforementioned ABS polymers are described at length in German Patent Application DE-A 19728629, which is hereby expressly incorporated by reference.

The aforementioned ABS polymers can have further typical adjuvants and fillers. Such substances are for instance lubricants or unmolding agents, waxes, pigments, dyes, flame retardants, antioxidants, stabilizers that protect against the influence of light, or antistatic agents.

The plastic material used for the rear injection in the method of the invention has long fibers in a quantity of in general 3 to 40 weight-%, preferably 7 to 25 weight-%, and in particular 10 to 20 weight-%. Examples of fibrous fillers that can be named are carbon, aramide or glass fibers, cut glass, or glass silk rovings. Glass fibers are especially preferred. As fibers, such natural fibers as flax, hemp, jute, sisal, ramie, or carnafl can also be used.

The glass fibers used can be of E-, A- or C-glass and are preferably equipped with a coat and/or an adhesion promoter. Their diameter is generally between 6 and 30 μm . Both endless fibers (rovings) and cut glass fibers (staple) with a length of 1 to 30 mm and preferably 3 to 20 mm, can be used.

In terms of the invention, the term "long-fiber-reinforced plastic material" can be used if the average fiber length in it is greater than or equal to 0.5 mm, preferably 0.7 mm, and especially preferably 1.0 mm (numerical averages). Long-fiber-reinforced plastic material also exists in particular whenever in the rear-injected molded part, as a rule at least 10 weight-%, preferably at least 30 weight-%, and especially preferably at least 50 weight-% of all the fibers have a length greater than 1 mm, and in particular greater than 1.5 mm. Suitable coats are composed for instance of aminosilanes, polyesters, or epoxy, polyurethane or phenol resins, or arbitrary mixtures of these coats, and they are available on the market either directly or are already applied by glass fiber manufacturers to the commercial glass fibers.

As particulate fillers, it is also possible to use soot, amorphous silicic acid, magnesium carbonate, powdered quartz, mica, bentonite, talcum, feldspar, or in particular such calcium silicates as wollastonite and kaolin.

For rear injection of composite laminated films with fiber reinforced plastic material, the plastic and fiber material, before the rear injection operation, are placed in an extruder or injection molding machine, which in the zone adjoining the compression zone has at least one distributive mixing element, and are melted and mixed. Preferably, all the plastic material downstream of the compression zone is in molten form. In extruders, the compression zone is also known as a transition zone (see among others Saechtling, *Kunststoff-Taschenbuch* [Plastics Handbook], 27th Ed., Carl Hanser Verlag, München, 1998, pp. 244-247).

As the distributive mixing elements, rhomboid or pinlike or camlike mixing parts or those with openings in the thread course can for instance be considered. Suitable mixing parts are also described in "*Einfärben mit Kunststoffen*" [Dyeing with Plastics], issued by VDI- Gesellschaft Kunststofftechnik, VDI-Verlag, Düsseldorf, 1975, pp. 261-265. As the mixing element, a separate mixing ring, which is disposed between the housing of the extruder or the injection molding machine (also called the stator) and the worm (also called the rotor), running freely around the worm, and is provided with circumferentially extending rows of openings, is preferably used, known for short as a Twente mixing ring. The openings can have regular or irregular geometric shapes but in general are circular or oval. They can moreover be disposed in random order or in encompassing circular paths on the mixing ring. The worm, that is, the rotor, can also have concavities under the mixing ring, which can both be made to coincide with the openings in the mixing ring and disposed offset from them. These concavities can match the openings in the mixing ring in terms of their circumferential shape, or can differ from them in size and shape. Typically, the concavities have the shape of partial cutouts of a ball or ellipsoid, that is, they are hemispherical or half-ellipsoid concavities, and a fluid transition from the rotor surface and concavity is preferred over an abrupt, sharp-edged transition. Especially suitable embodiments of extruders or injection molding equipment containing a separate mixing ring that has openings are also described EP 340 873 B1 and German Patent DE 42 36 662 C2, which are hereby expressly incorporated by reference into the present disclosure.

The production of the film rear-injected plastic molded parts is preferably accomplished in a multistage process, by

- a) producing the film, in particular the composite laminated film, by means of adaptor or nozzle (co)extrusion of the cover, substrate layer and optionally intermediate layer, with the entire film composite preferably produced in a single-stage process;
- b) optionally, thermoforming of the composite laminated film in a forming tool; and
- c) rear injection of the composite laminated film with the fiber reinforced plastic

material; the plastic material and fiber material is placed before the rear injection in an extruder or injection molding machine, which in the zone adjoining the compression zone has at least one distributive mixing element, and melted and mixed.

The plastic molded parts according to the invention can be used in the motor vehicle field, especially as exterior motor vehicle body parts, for instance for such relatively small exterior motor vehicle body parts as mirrors or visors, or for such large-area exterior body parts as fenders, hoods, coverings, doors, or bumpers. However, applications for instance as inner lining parts of motor vehicles, such as door side panels, A, B and C pillar and steering column linings, dashboards, and lining components in the foot area of motor vehicles can be considered, as well as applications as interior components for aircraft, interior components for ships, housings of household appliances and electric appliances, outdoor furniture, battery carriers, casement sections, curtain walls, doors, floor coverings, mobile telephone housings or shells for chairs.

The molded parts according to the invention have a very satisfactory breaking behavior and very good impact strength even at low temperatures. This is particularly true if ABS polymers are used as rear injection material. No unevenness and in particular no glass pits are observed on either the film side or the back side of the film rear-injected molded part, even in a climate change test.

Finally, by the method of the invention, plastic material reinforced with long fibers can be obtained by homogeneously incorporating fiber material directly into the plastic material. Unlike conventional methods, even in large-scale production it is no longer necessary to incorporate the long fibers into the plastic material by way of a polymer granulate or polymer pellets containing long fibers. Instead, the fiber material and plastic material can be mixed cold before being added to the extruder. It is equally possible to add the fiber material separately to the polymer granulate that is located in the mixing and melting device, such as an extruder. The polymer granulate can be in molten, partly molten, or nonmolten form.

The surface of the molded parts according to the invention is unimpaired by the use of fiber reinforced products. For example, rear-injected products of ABS polymers reinforced with long glass fibers (average fiber length in the component approximately 0.7 to 2 mm, by average weight) have a satisfactory surface. Fibers do not show even on the side not coated with film.

In mechanical tests, such as the head impact test, rear-injected specimens produced with long-fiber-reinforced plastic material, such as ABS polymer, exhibit very good breaking behavior and very good toughness, and in particular even at low temperatures. With an average fiber length of 0.7 mm (average weight) in the plastic material, very good

mechanical properties are already found, especially in terms of breaking behavior and toughness.

The combination of long-fiber-reinforced plastic materials, particularly ABS polymer, as rear-injected material (thickness preferably 2 to 3 mm) with a composite laminated film of unreinforced polymers makes it possible to produce Class A components that can be produced without needing to be painted and that have a modulus of elasticity greater than 3000 and preferably greater than 3200 MPa, and a longitudinal thermal expansion of less than 50 e-6 1/K and also have a nonsplintering breakage pattern at low temperatures. The breakage pattern after the head impact test at -30°C is even more favorable than when an unreinforced thermosetting plastic is used.

The invention will be explained further in terms of the following examples.

Examples:

The rear-injected molded parts were produced with an injection molding machine of the Krauss Maffei 1500 type. In the variant of the invention, a standard three-zone worm with a diameter of 115 mm and a Twente mixing ring made by Maas International (Wierden, Netherlands) was used. In the variant not according to the invention, a conventional standard three-zone worm made by Krauss Maffei with a diameter of 105 mm was used. The temperature profile of the injection molding machines was as follows: 210/250/260/260/260°C.

For the rear injection, the commercial product Terluran® weight-% 22 (BASF AG) was used as the ABS plastic material (I).

The following glass fibers (II) were used:

- i) Cratec® 152A-14C (13 mm cut length, Owens Corning),
- ii) Cratec® 183F-11C (4 mm cut length, Owens Corning).

The rear-injected film (III) was composed of a substrate layer (1) as a supporting film (900 µm) of a commercially available ASA copolymer (Luran® S, BASF AG), and a cover layer (3) (100 µm), also from a commercially available polymethyl methacrylate (Lucryl®, BASF AG).

The components of the individual layers (1) and (3) were each melted separately in an extruder at 230 to 250°C and homogenized. The melt flows were placed on one another in a feedblock before entering the wide-slot nozzle and stretched as a layer composite to the

nozzle width (1.2 m).

The ABS material (I) and the glass fiber material (II i) and ii)) (15 weight-%, referred to fiber reinforced ABS polymer) were fed, cold-mixed, into the injection molding machine. Via an injection molding tool in which the composite film (III) had been positioned, motor vehicle hatchback panels 400 x 1200 x 3.2 mm in size were produced.

The other findings are summarized in Table 1 below.

Table 1

Example	Glass Fiber (II)	Glass Surface ^b	Impact Strength (kJ/m ²)	Tensile Strength (Mpa)	Elongation to Break (%)
1	i)	-very good	20	52	2.7
2 ^{a)}	ii)	+/poor	18	51	2.9
3 ^{a)}	i)	+/poor	19	48	2.6
4 ^{a)}	Ultradur® S 4090 G6	-/very good	18	40	1.1

a) Comparison example

b) The rear-injected comparison molded parts of Examples 2 and 3 were produced conventionally, without using the mixing part. They had glass pits on the side remote from the film, and on the film side these pits were quite noticeable in a climate change test at temperatures in the range from -40 to +90°C. In the climate change test, Example 1 showed neither impairment or change in the satisfactory surface nor any worsening in mechanical properties.

The comparison molded part of Example 4, also made without using the mixing part, in which the glass fibers have an average length of about 0.3 mm in the polymer matrix (average weight), have a markedly lower elongation to break and markedly less tensile strength compared to components according to the invention. Here the glass fibers, embedded into a polymer granulate or in other words in the form of tiny rod-shaped granules, was worked into the polymer matrix to be melted.

The climate change test was performed under the following conditions which are usual for automobile components: 3 cycles of 15 hours each at 90°C, 30 minutes at 23°C, 8 hours at -40°C, and 30 minutes at 23°C.

The impact strength was determined in accordance with ISO 179/1eU, using specimens 80 x 10 x 3.2 mm in size cut mechanically out of the hatchback panels.

The tension tests were performed in accordance with ISO 527-2 at 23°C, with a take-

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off speed of 5 mm/min.

Claims

1. A method for producing molded plastic parts with a rear-injected foil, consisting of a foil and a long-fiber-reinforced plastic material, wherein the foil is positioned in a molding tool and a fiber-reinforced plastic material is rear-injection molded to constitute a molded part, characterized in that prior to the rear injection molding process in an extruder or an injection molding machine, which have at least one distributive mixing element in a zone following the compression zone, the plastic material and the fiber material are melted and admixed.
2. The method in accordance with claim 1, characterized in that the mixing element is a separate mixing ring, which is disposed between the housing of the extruder or of the injection molding machine (stator) and the worm (rotor), running freely around the worm, and is provided with circumferentially extending rows of openings; and that the worm has concavities under the mixing ring.
3. The method in accordance with claim 1 or 2, characterized in that the film is a composite laminated film, including in this order at least one substrate layer, optionally at least one intermediate layer, and at least one transparent cover layer.
4. The method in accordance with claim 3, characterized in that the composite laminated film includes the following:
 - a) a substrate layer (1), containing ASA polymers, ABS polymers, polycarbonates, polyesters, polyamides, polyether imides, polyether ketones, polyphenylene sulfides, polyphenylene ethers, or mixtures thereof;
 - b) optionally, an intermediate layer (2), containing poly(meth)acrylate, high-impact poly(meth)acrylate, poly(meth)acrylamide, poly(meth)acrylonitrile, ASA polymers, ABS polymers, polycarbonates, polyesters, polyamides, polyether sulfones, polysulfones, polyvinyl chloride, or mixtures thereof; and
 - c) poly(meth)acrylates, high-impact poly(meth)acrylates, fluoro(co)polymers, ABS polymers, polycarbonates, polyethylene terephthalate, amorphous polyamide, SAN polymers, polyether sulfones, polysulfones, or mixtures thereof.
5. The method in accordance with claim 3 or 4, characterized in that the substrate layer is essentially constructed from ASA polymers and optionally polycarbonates.
6. The method in accordance with claims 3 to 5, characterized in that ASA polymers

are essentially composed of the following:

- a) 1 to 99 weight-% of a graft copolymer (component A) comprising
 - a1) 1 to 99 weight-% of a particulate graft foundation A1 comprising the monomers,
 - a11) 80 to 99.9 weight-% of at least one C₁ to C₁₈ alkyl ester of acrylic acid as component A11,
 - a12) 0.01 to 20 weight-% of at least one polyfunctional cross-linking monomer as component A12,
 - a2) 1 to 99 weight-% of a graft overlay A2 comprising the following monomers, referred to A2,
 - a21) 40 to 100 weight-% units of styrene, a substituted styrene, a (meth)acrylic acid ester, or mixtures thereof, as component A21, and
 - a22) 0 to 60 weight-% units of acrylonitrile or methacrylonitrile, as component A22, in which the graft overlay A2 comprises at least one graft sheath, and the graft copolymer has a mean particle size of 50 to 1000 nm; and
- b) 1 to 99 weight-% of a copolymer (component B) comprising
 - b1) 40 to 100 weight-% units of styrene, of a substituted styrene, or of a (meth)acrylic acid ester or mixtures thereof, as component B1, and
 - b2) up to 60 weight-% of acrylonitrile or methacrylonitrile, as component B2.

7. The method in accordance with claims 1 to 6, characterized in that an ABS polymer, polybutylene terephthalate, or a mixture of polycarbonate and polybutylene terephthalate or of an ASA polymer and polycarbonate or of an ASA polymer and polybutylene terephthalate is used as the plastic material.

8. The method in accordance with claims 1 to 7, characterized in that the fibers in the rear-injected plastic molded part have an average fiber length greater than or equal to 0.5 mm (numerical average).

9. Rear-injected molded plastic parts obtained in accordance with one of claims 1 to 8.

10. Use of the molded plastic parts in accordance with claim 9 as interior or exterior

auto body components, interior components for aircraft, interior components for ships, housings of household appliances and electric appliances, outdoor furniture, battery carriers, casement sections, curtain walls, doors, floor coverings, mobile telephone housings or shells for chairs.